# Feasibility of Using a Galvanic Cell Array for Corrosion Detection and Solution Monitoring

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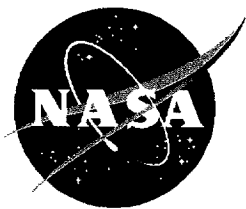- CONTRACTOR REPORT. Scientific and technical findings by NASA-sponsored contractors and grantees.

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# ABSTRACT

This effort is directed towards developing an electrochemical sensor to analyze the corrosive nature of the surface of Mars. There have been discussions among planetary scientists that the subsurface of Mars is a brine-like mixture. Based upon these suppositions, it is anticipated that the sensor will be integrated into an advanced electronic tongue that will be used in a subsurface explorer being developed at NASA/JPL.

The current version of the electronic tongue is an outgrowth of a 25-cm$^3$ electrochemical cell originally designed for the Mars Environmental Compatibility Assessment (MECA) project, which utilized an array of 20 prefabricated ion selective electrodes. In its current configuration, the device is capable of performing measurements using standard electrochemical techniques, which include cyclic voltammetry (CV) and anodic stripping voltammetry (ASV). An additional component, consisting of an array of galvanic cells, has been added based upon potentiostatic polarization measurements in various electrolytes.

In this new design, a series of anodic materials and a single cathodic metal (zinc) is exposed to various electrolytes. When the two dissimilar metals are inserted into the Martian soil, the metals act as electrodes and the brine acts as an electrolyte creating a galvanic cell. When in contact with the electrolyte, a short circuit current is generated at a prescribed voltage ($E_{couple}$), which is unique for each anodic material. From these $E_{couple}$ values and the responses of the individual galvanic couples, it is possible to speculate upon the nature of the electrolyte. Furthermore, conclusions into the corrosive nature of the media can be made based upon the correlation between measured corrosion currents ($I_{couple}$) from potentiodynamic scans and corrosion rate values.

An investigation into the response of the individual galvanic couples was conducted using potentiodynamic polarization measurements of solutions under conditions of varying corrosivity. It is hypothesized that the differing electrodes may provide a means to further investigate the corrosive nature of the analyte through genetic algorithms and pattern recognition techniques. The robust design of the electrochemical sensor makes its utilization in space exploration particularly attractive. Since the electrodes are fired on a ceramic substrate at 900 °C, they may be one of the most rugged sensors available for the anticipated usage.

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# ACRONYMS AND SYMBOLS

## Acronyms

| | |
|---|---|
| ASV | anodic stripping voltammetry |
| CV | cyclic voltammetry |
| CR | corrosion rate (cm/s) |
| CDDF | Center Director's Discretionary Fund |
| DI | deionized |
| FHWA | U.S. Federal Highway Administration |
| ISE | ion selective electrode |
| JPL | Jet Propulsion Laboratory |
| KSC | Kennedy Space Center |
| MECA | Mars Environmental Compatibility Assessment |
| MOC | Mars Orbital Camera |
| NACE | National Association of Corrosion Engineers |
| NASA | National Aeronautics and Space Administration |
| OCP | open circuit potential |
| PDS | potentiodynamic scan |
| VGAR | voltage galvanic auxiliary vs reference |
| VGRW | voltage galvanic reference vs working electrode |
| ZIF | zero insertion force |

## Standard Symbols

$A$ = area of the electrode ($cm^2$)

$°C$ = degree Celsius

$e^-$ = electron

$E$ = applied potential (V)

$E_{couple}$ = coupled corrosion potential (V)

$E_{corr}$ = corrosion potential (V)

$E'_M$ = equilibrium potential for metal reaction

$E'_X$ = equilibrium potential for reduction reaction(s)

$F$ = Faraday constant

$i_{corr}$ = corrosion current density ($A/cm^2$)

$I_{couple}$ = coupled corrosion current density ($A/cm^2$)

$I_{corr}$ = corrosion current (A)

$I_{couple}$ = coupled corrosion current (A)

$I_{e,x}$ = external current (A)

$I_{ox,M}$ = oxidation current for metal (A)

$I_{red,X}$ = reduction current (A)

$I_{o,M}$ = exchange current for reaction $M = M^{m+} + m$ (A)

$I_{o,X}$ = exchange current for reduction reaction $X^{x+} + x = X$ (A)

$M$ = generic symbol used to represent a metal

MW = molecular weight of metal, (g/mol)
*m* = oxidation state or valence of metal (atomic weighted values are used for alloys)
mV = millivolt
n = integral number
$R_p$ = polarization resistance (Ohms)
X = notation used to represent a generic element or compound


## Greek Symbols

$\beta_{ox,M}$ = slope of oxidation overpotential curve (V – log decade)
$\beta_{red,x}$ = slope of reduction overpotential curve (V – log decade)
$\rho$ = density of metal (g/cm$^3$)


## Chemical Symbols

Au = gold
Ag = silver
Cu = copper
Fe = iron
$H^+$ = hydrogen ion
$H_2$ = hydrogen gas
$H_2O$ = water
$H_2SO_4$ = sulphuric acid
KCl = potassium chloride
NaCl = salt
$NaNO_3$ = sodium nitrate
Ni = nickel
$O_2$ = oxygen
$OH^-$ = hydroxide ion
Pd = palladium
Pt = platinum
Ru = ruthenium
Sn = tin
Zn = zinc

# 1    INTRODUCTION

## 1.1    CORROSION

A recent study (completed in 2002) conducted by CC Technologies Laboratories, Inc., with support from the U.S. Federal Highway Administration (FHWA) and the National Association of Corrosion Engineers (NACE) reveals that the cost of corrosion in the United States was an astonishing $276 billion in 1998. This translates to approximately 3.1% of the U.S. Gross Domestic Product.[1] It has been estimated that approximately 25 to 30% of the corrosion costs that were incurred in the United States could have been prevented. Individual sectors of the economy were referenced in the report, which stated that corrosion cost $47.9 billion to utilities, $29.7 billion to transportation, $22.6 billion to infrastructure, and $20.1 billion to government agencies.[1] Corrosion monitoring before the onset of corrosion is necessary to minimize these costs.

The Kennedy Space Center is a Government facility particularly susceptible to corrosion-related problems because of the increased quantities of chloride ions from the oceanic environment. Further problematic to the structures at KSC is the acidic exhaust deposited by the Space Shuttle. Finally, the Florida sunshine heat and humidity combine to accelerate corrosion and breakdown protective coatings.

Great strides have been made to protect the facilities from corrosion. Older facilities are continuously being updated with materials that are more resistant to corrosion. As new facilities are being built, they are made from materials specifically chosen to resist corrosion. The newer structures are often able to resist corrosion and therefore reduce the annual cost associated with corrosion damage. Unfortunately, an increased lifespan through the reduction of corrosion merely extends the onset of the destructive process. Therefore, many of the corrosion-related problems prevalent with the older infrastructure can occur with currently built facilities but after a longer span of time. While the deleterious effects of the process can be reduced, it is often impossible to stop entirely.

The investigation of a multicomponent sensor to test corrosivity and conductivity was undertaken to address the need for corrosion detection prior to the onset of serious corrosion-related problems. Further applications to the protection of space-based crafts, facilities, and structures are anticipated.

## 1.2    APPLICATIONS FOR THE ANALYSIS OF MARTIAN SOIL

The analytical determination of the components that comprise Martian soil is a complex assignment. A device designed to accomplish this task must consist of a set of sensing components, which have the ability to analyze the environment for multitude chemical constituents that exist on the planet. At the same time, the device must be capable of withstanding the environmental extremes that not only exist in the cold extraterrestrial environments of space, but also in the hot and humid launch pad conditions prevalent at the Kennedy Space Center. In the process, the device must withstand the harsh acceleration and vibrations present at launch. The development of a device that satisfies all these conditions is daunting at best.

It has been hypothesized that environmental conditions on Mars were perhaps favorable to support biological activity at one time.[2,3] Interest in the concept of biological activity on Mars grew with evidence provided by the Mars Orbital Camera (MOC) that water may be present on the planet.[4,5] Figure 1 is a picture from the MOC that provides visual evidence that gullies may have formed as the result of water-induced erosion.

The elemental composition of the planet was investigated by the Viking Landers, as well as the Sojourner rover's x-ray spectrometers. The analysis suggested a salt-rich environment consisting of cationic species of silicon, iron, aluminum, and magnesium as major constituents.[6] The elements are principally thought to exist as oxides, though sulfates[7] and carbonates[8] are thought to exist on the surface of the planet as well. Curiously, the Viking experiments indicate that the exposed surface of the planet is devoid of carbon-containing molecules.[8]

Paramount to this investigation is the presumption that the Martian surface contains high concentrations of inorganic salts. The significance of the chemical composition lends credence to the feasibility of utilizing electrochemical methods of analysis. While specifically designed for the analysis of Martian soil, the multisensing components allow for the analysis of aqueous samples, which are not necessarily related to the exploration of the Martian environment.

## 2    ELECTROCHEMICAL MULTISENSING CERAMIC

## 2.1    OVERVIEW OF SENSING ELECTRODES

The electrochemical sensor under development is an extension of the Mars Environmental Compatibility Assessment (MECA) project.[6] The device (Figure 2) was designed to perform electrochemical measurements including cyclic voltammetry (CV), anodic stripping voltammetry (ASV) and conductometric analysis (Figure 2). Improvements on the original MECA design have been made prior to this investigation and have been reported elsewhere.[6,9-12]

In its updated version, a galvanic cell array has been added as an additional component to investigate the corrosivity of aqueous solutions and soil samples (Figure 2). It is anticipated that the sensor will be incorporated into a subsurface explorer designed at NASA/Jet Propulsion Laboratory (JPL). The underground motion of the probe is based upon an innovative percussion mechanism known as a spinning hammer. The concept uses a high-speed electric motor, spinning shaft, and a hammer that translates rotational motion into translational kinetic energy.[9,11]

For the galvanic cell array to be successful, the soil must facilitate the movement of current. In recent months, a great deal of discussion has centered upon the makeup of the surface of Mars. Specifically, the subsurface is thought to consist of a brine-like mixture of salts.[9] This should decrease the resistivity across the interface between the electrodes making electrochemical measurements feasible for analytical determinations.

## 2.2    ION SELECTIVE ELECTRODE (ISE) ARRAY

Figure 2 shows the three major components of the electrochemical sensor. The first element discussed is the ISE array (shown on the far right of Figure 2). It is the result of a joint collaboration with Tufts University and NASA/JPL.[11] In general, ion selective electrodes are used to identify analytes based upon a potentiometric determination across barrier membranes. The ion selective electrodes for the MECA project were based upon commercial polymer membrane and solid pellet technologies developed at ThermoOrion Research.[12]

The use of ion selective electrodes in this multisensing version builds upon the MECA project. Of importance to the investigation is the implementation of fabrication techniques necessary to decrease the size of the ion selective electrodes to the point that a large number can be arrayed in a small space.[11] The multiplicity of electrodes will extend the number of analytes that can be detected by the ISE components.

## 2.3    CYCLIC VOLTAMMETRY (CV) AND ANODIC STRIPPING VOLTAMMETRY (ASV) ELECTRODES

The second major component of the multisensing device is shown in the center of Figure 2. The electrodes are used to perform CV and ASV experiments. CV is an experimental technique in which a potential waveform is varied, and a current that is based upon the oxidation or reduction characteristics of the analyte in solution is measured. ASV is a complimentary technique, in which a sufficiently negative potential is used to reduce ions in solution onto an electrode surface. After a set period, the potential is increased to values that are more positive and the analyte is reoxidized. The currents generated from the oxidation and reduction reactions can then be qualitatively and quantitatively measured.[10]

Ordinarily, electrochemical measurements utilize a three-electrode system. Often, the electrode of interest is the working electrode. This electrode is often inert for most electrochemical studies and is the electrode in which the electrochemical reactions in solution are measured. In the present configuration, the working electrode used for CV and ASV measurements is made from an Au/Pt ink annealed in air at 850 °C.

The counter electrode (auxiliary electrode) is a metal species that serves to support the electrochemical processes. Ordinarily, the metal is inert. In this case, the counter electrode is made from an Au/Pt ink as well. This electrode supports the oxidation and reduction reactions in solution, without itself taking part by corroding. Finally, the reference electrode serves as a standard by which the potential of the working electrode can be measured. The quasi-reference electrode used for CV and ASV measurements is made from an Ag/Pd ink fired at 850 °C in air.

## 2.4    GALVANIC CELL ELECTRODES

### 2.4.1    GALVANIC CORROSION

Individually, a metal corrodes through a redox reaction in which the metal species undergoes oxidation. Galvanic corrosion is a form of corrosion that increases the rate of oxidation of a metallic surface. Figure 3 illustrates the three components needed for the process to occur. The

first element needed is two metals of differing half-cell potentials. The second is a conducting medium such as soil or water. Finally, the third component that is necessary is electrical contact between the metal samples to complete the electrochemical circuit.

When galvanic corrosion occurs, the metal with a more positive or noble corrosion potential forms the cathode, while the metal with the more negative or active corrosion potential forms the anode. The anodic metal will corrode to a greater extent than it would by itself in the same electrolyte. The cathodic metal will have galvanic protection.

When the galvanic couple of differing metals is placed into a conducting solution, a corrosion potential results that differs from the corrosion potential of either of the metals by themselves. Thus, the corrosion potentials for the individual metals ($E_{corr}$), are shifted to a new value ($E_{couple}$). In this scenario, the metal with the more negative uncoupled corrosion potential experiences an increase in the corrosion rate, whereas the metal with the more positive corrosion potential experiences a decrease in the corrosion rate. From a Tafel plot analysis, it is possible to determine the $I_{couple}$ value, which is the corrosion current for the system and which is the sum of the corrosion current for the individual metals.[13]

$$I_{couple} = \sum I_{ox} = \sum I_{red} \qquad (1)$$

## 2.4.2 GALVANIC CELL DESIGN

The galvanic cell approach is an extension of the standard electrochemical techniques used with the center electrodes and is illustrated in the left of Figure 2. The galvanic cell design is loosely based upon the work of Bennett and Greene in which potentiostatic determinations of various galvanic couples were investigated in solutions of 1 normal sulfuric acid and 3 percent sodium chloride.[14] Potentiostatic polarization involves maintaining an electrode at a series of fixed potentials and measuring the resulting current. For this work, potentiodynamic polarization measurements were utilized. The technique is similar to the potentiostatic method but differs in that it uses a sweeping potential through a preset range of voltages. This method was chosen based upon the increased rate of data collection associated with the technique. In theory, potentiodynamic plots are useful to investigate corrosion rates, pitting susceptibilities, and the passivity of metals.

The galvanic cell concept employed in the current sensor uses a series of cathodic metals and a single anodic metal (zinc – which is represented by the outer ring of each galvanic cell in Figure 2). When the two metals are brought into contact with a conducting medium, the two metals act as electrodes and the conducting solution or brine acts as an electrolyte, thereby creating the galvanic cell. The current is measured as the potential is scanned from a sufficiently negative value. At a given voltage, a short circuit current is reached at which the oxidation (corrosion) and reduction processes of the metal are equal in magnitude. The voltage at which these short circuit currents occur can be unique for each anodic material investigated. From the potentiodynamic plots, the corrosion current for the galvanic couple ($I_{couple}$) can be obtained through a Tafel plot analysis.

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# 3    COMPONENTS OF THE ELECTROCHEMICAL SENSOR

## 3.1    CERAMIC SUBSTRATE

In contrast to the MECA wet chemistry laboratory,[6] the current ceramic design was fabricated in a planar arrangement to facilitate the cleaning of the surface of the electrodes. This design has been selected based upon the ease with which soil samples can be analyzed and the analyte discarded prior to further determinations.

A picture of the sensing ceramic is shown in Figure 4. The image clearly shows the three components that were previously discussed, as well as the U-shaped thermometer at the top of the figure, the miniaturized heater near the center, and the conductivity electrodes at the bottom. The ceramic is 3.3-cm in diameter and is 1-mm thick. The device is constructed using technology similar to that used to fabricate microelectronics on co-fired ceramic substrates.[15]

To construct the sensing electrodes, various inks were screen printed onto the ceramic substrates to form four duplicate galvanic cells (left side of Figure 4). The screen-printing process utilized a series of templates to mask regions of the ceramic substrate, after which metallic inks were applied to ultimately form the electrodes. The outermost electrode (counter or auxiliary) is fabricated from a zinc-rich metallic ink. This electrode is common to all the galvanic cells. The cathodic working electrodes are the rings of differing colors that are made by screen-printing different metallic inks (Sn, Cu, Fe, Ni, Au/Pt, and $RuO_2$). The reference electrode, located in the center of each cell, is fabricated from a Pd/Ag ink. The inks were fired at a temperature of 850 °C in air, except for the Cu and Ni electrodes that used a nitrogen atmosphere. This process results in an electrochemical sensor that is extremely robust.

## 3.2    EXPERIMENTAL APPARATUS

Figure 5 shows the two sample chambers that were fabricated for use with the ceramic substrates. The open sample chamber shown on the left side of the figure was designed to analyze soil samples. The fluidics chamber on the right side of the same figure was designed for use with aqueous samples. The tube connected to the right-hand side of the fluidics chamber leads to the pump that is located on the fluidics board as shown on the bottom of Figure 6. The pump is capable of drawing from any of eight inlets and extends the capabilities of the instrument by allowing for multiple samplings.

Both sample chambers were designed with O-rings that make contact with each side of the ceramic. The O-rings are not only meant to seal the chambers but also to cushion the ceramic from harsh environmental influences such as those experienced during launch. A series of 0.5-mm diameter stainless-steel pins protrude from the back of the ceramic substrate, run through the deposition chamber, and make electrical contact through the zero insertion force (ZIF) socket located on the top circuit board in Figure 6.

## 3.3 DEPOSITION CHAMBER ELECTRONICS

Figure 6 shows a resistor card mounted in the ZIF socket on the electronics circuit board. The resistor card is used to test the functionality of the electronics and verify that the system is working properly. With the resistor card in place, a potential scan is initiated and the current is recorded as a function of applied potential. Figure 7 shows the circuitry used to make normal potentiodynamic determinations with the galvanic cell array. In principle, the device is similar to that for ordinary electrochemical measurements and is based upon the three-electrode system described previously.

Customary electrochemical determinations focus on redox properties at the working electrode. For the application reported here, the working electrode consists of the cathodic metal of interest. This investigation is less concerned with the actual reactions in solution and more interested in how the solution influences the corroding metal. The reference electrode is used as a standard to measure the potential of the working electrode. In the potentiodynamic mode, the voltage is scanned from negative to positive values and is a function of the potential difference between the reference and working electrode. In the circuit diagram in Figure 7, the notation voltage galvanic reference vs working electrode (VGRW) represents the potential of the working electrode with respect to the reference electrode. The notation voltage galvanic auxiliary vs reference (VGAR) represents the galvanic voltage of the auxiliary (or counter) electrode with respect to the reference electrode. For laboratory measurements, the auxiliary electrode is often an inert metal such as platinum, and merely serves as a conductor to complete the electrochemical circuit. Based upon the work of Bennett,[14] a more reactive metal species was chosen for the auxiliary electrode to form a galvanic cell. This concept allows corrosive processes to occur on both electrodes and is the model upon which the investigation is based.

## 4. CORROSION AND MEASUREMENT TECHNIQUES

### 4.1 CORROSION

Corrosion is the result of the deterioration of a metal due to a reaction with its environment. The anodic reaction normally used to represent this process is:

$$M \rightarrow M^{n+} + ne^-$$ (2)

For the anodic oxidation to occur, cathodic reactions must be present to consume the electrons liberated by the anodic corrosive process. These reactions may include, but are not limited to:

The reduction of water:
$$2H_2O + 2e^- \rightarrow H_2 + 2OH^-$$ (3)

The reduction of an acid:
$$2H^+ + 2e^- \rightarrow H_2$$ (4)

Oxygen reactions:
$$O_2 + 2H_2O + 4e^- \rightarrow 4 OH^-$$ (5)

$$O_2 + 4H^+ + 4e^- \rightarrow 2\,H_2O \qquad (6)$$
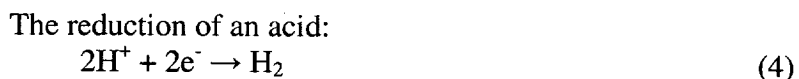
## 4.2    OPEN CIRCUIT POTENTIAL MEASUREMENTS

For a system in which a metal is simply immersed in a conductive solution with no applied potential, the voltage that is measured is called the open circuit potential (OCP). Typically, for a system such as this, the metal is oxidized (corrodes) and the solvent or electrolyte is reduced. At the OCP, the rate of oxidation and reduction reactions is equal, the metal corrodes freely, and the OCP is the potential that is measured. Unfortunately, the external current (the measured current) is zero.[13] If it were possible to determine the current associated with the oxidation of the metal, it would be possible to calculate the corrosion rate.

## 4.3    POTENTIODYNAMIC MEASUREMENTS

Corrosion is an electrochemical process. Therefore, electrochemical techniques are often used to accelerate and monitor corrosive processes for investigative purposes. An electrochemical technique of particular interest is potentiodynamic polarization. The method measures current as a function of applied potential. A hypothetical plot is shown in Figure 8.

Two half-cell reactions are of particular interest when corrosion processes are studied: The reduction half reaction, which is shown in generic form in equation 7, and the oxidation of a metal (shown in equation 2).

$$X^{n+} + ne^- \rightarrow X \qquad (7)$$
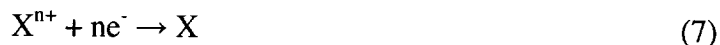
When a potential is applied through an external means (with the use of a potentiostat), the current potential profile of the oxidative and reductive processes occurs by:

$$I_{ex} = I_{o,M}\,e^{2.3(E-E'_M)/\beta_{ox,M}} - I_{o,X}\,e^{-2.3(E-E'_X)/\beta_{red,X}} \qquad (8)$$

This constitutes the Tafel relationship utilized in potentiodynamic polarization measurements and describes the current produced with the application of a specified potential for a particular set of reactions. In essence, the external current ($I_{ex}$) is the difference of the current resulting from the oxidation of the metal and the reduction of species in the medium being analyzed. $I_{o,M}$ and $I_{o,x}$ are the oxidative and reductive currents for the half reactions pertinent to the system being analyzed, $E$ is the applied potential, and $E'_M$ and $E'_X$ are the anodic and cathodic reaction potentials. Finally, $\beta_{ox,M}$ and $\beta_{red,X}$ are the slopes of the oxidation and reduction overpotential curves.

Ordinarily, potentiodynamic scans are initiated at values negative of the corrosion potential. For this reason, open circuit measurements are often run immediately preceding the potentiodynamic scans to determine the corrosion potential of the system. At potentials more negative of the OCP, more electrons are consumed by the reductive processes in solution than are produced by the corrosive oxidative influences at the working electrode. When the potential is scanned to values more positive than the OCP, more electrons are produced through the oxidation of the metal than are consumed by the reduction reactions in solution. Extrapolation of the data results

in straight lines that form the anodic and cathodic branches of the potentiodynamic plot (Figure 8).

Between the anodic and cathodic regions, the external current ($I_{ex}$) becomes zero, and $I_{ox,M} = I_{red,X}$. The potential at which this occurs is the corrosion potential ($E_{corr}$) of the system. The measured corrosion potential gives an indication of the corrosivity of the system. Unfortunately, in order to calculate corrosion rates, the corrosion current ($I_{corr}$) must be obtained.

The Tafel expression with $E_{corr}$ and $I_{corr}$ as parameters allows for the determination of $I_{corr}$ through:

$$I_{ex} = I_{corr}[e^{2.3(E-E_{corr})/\beta_{ox,M}} - e^{-2.3(E-E_{corr})/\beta_{red,x}}] \tag{9}$$

This equation results in the anodic and cathodic Tafel regions plotted as dashed lines in Figure 8.[13]

Once the corrosion current is determined, the corrosion current density can be calculated by dividing the current by the area of the electrode:

$$i_{corr} = \frac{I_{corr}}{A} \tag{10}$$

Finally, the corrosion current density permits the determination of the corrosion rate (CR) through the relationship.[13]

$$CR = \frac{MW \cdot i_{corr}}{m \cdot F \cdot \rho} \tag{11}$$

The applicable parameters are the molecular weight of the corroding metal (MW), the corrosion current density ($i_{corr}$), oxidation or valence of the corroding metal (m), the density of the metal ($\rho$) and Faraday Constant (F).

## 4.4    POLARIZATION RESISTANCE

Polarization resistance is a linear approximation of the slope of the potential current relationship near $E_{corr}$, when plotted on a linear axis, and provides an additional technique to determine corrosion current values. In general, the linearity exhibited in the potential-current relationship holds within a few millivolts of $E_{corr}$.

The Stern-Geary relationship[16,17] defines the polarization resistance ($R_p$) as a function of the corrosion current and Tafel slopes as given by:[18]

$$Rp = \frac{\beta_{ox,M} \cdot \beta_{red,X}}{2.3 \cdot i_{corr}(\beta_{ox,M} + \beta_{red,X})} = \frac{B}{i_{corr}} \tag{12}$$

Therefore, $R_p$ can be experimentally determined by calculating the slope of the tangent line near zero current, and the corrosion current density can be calculated by:

$$i_{corr} = \frac{B}{R_p}$$

(13)

This results in the inverse relationship between $R_p$ and $i_{corr}$ for the system.

## 4.5    GALVANIC CORROSION

Individually, a metal corrodes through a redox reaction in which the metal species undergoes oxidation. Galvanic corrosion is a form of corrosion that increases the rate of oxidation of the metallic surface. Figure 8 illustrates the three components needed for the process to occur. The first component needed is two metals of differing half-cell potentials. The second is a conducting medium such as soil or water. Finally, the third component that is necessary is electrical contact between the metal samples, which completes an electrochemical circuit.

When galvanic corrosion occurs, the metal with a more positive or noble corrosion potential forms a cathode, while the metal with the more negative or active corrosion potential forms the anode. The anodic metal will corrode to a greater extent than if it were by itself in the same electrolyte. The cathodic metal will have galvanic protection.

When galvanic couples of differing metals are placed into a conducting solution, a corrosion potential results, which differs from the corrosion potential of either of the metals by themselves. Thus, the corrosion potentials for the individual metals ($E_{corr}$), are shifted to a new value ($E_{couple}$). In this scenario, the metal with the more negative uncoupled corrosion potential experiences an increase in the corrosion rate, whereas the metal with the more positive corrosion potential experiences a decrease in the corrosion rate. From a Tafel plot analysis, it is possible to determine the $I_{couple}$ value, which is the corrosion current for the system and which is the sum of the corrosion current for each of the individual metals.[13]

$$I_{couple} = \sum I_{ox} = \sum I_{red}$$

(14)

Bennett and Jones suggested the use of potentiostatic polarization diagrams to predict the galvanic current ($I_{corr}$) for a metal couple[14,18] using the anodic and cathodic polarization curves for each metal. An extrapolation of the polarization data from the individual metals, could then be used to predict the potential current relationships for the coupled galvanic metals. Potentiostatic polarization diagrams were obtained for metals in aerated 3% NaCl and dearated 1N $H_2SO_4$. This investigation was based on the mixed potential theory, which states that the sum of the oxidation and reduction reactions of a system are equal.[13,14] A collection of polarization curves for the individual oxidation and reduction reactions in standard solutions were assembled. From the potential-current relationships of each system, the mixed potential of the galvanic system could be determined. Specifically, the intersection of the reduction curve for the more noble metal and the oxidative curve for the more active species resulted in potential-current relationships that were used as a predictive model to investigate the galvanic attack of the coupled metals in similar solutions.

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Bennett and Jones determined the mixed couple galvanic relationships for a series of metals in standard solutions.[14,18] This lead to the concept of using a series of galvanically coupled metals to investigate the corrosivity of various solutions. In order to implement this idea, an electro-chemical sensor was developed to analyze the corrosive nature of the brine present under the sur-face of Mars. In this methodology, current is measured as a function of an applied potential for duplicate galvanic couples. The working electrode consisted of screen-printing metallic inks (Sn, Cu, Fe, Ni, Au/Pt and $RuO_2$), and an active metal (Zn) forming the other half of the galvanic couple.

It was hypothesized that the differing electrodes could provide a means to further investigate the corrosive nature of an analyte based upon the short circuit potential, the $E_{couple}$ and the $I_{couple}$ val-ues. Specifically, the $E_{couple}$ values of the mixed couple can be used to give a vicarious indica-tion into the corrosivity of a solution. Thus, the two corrosion potentials $E_{corr}$ are shifted to a new value ($E_{couple}$). In this scenario, the metal with the more negative uncoupled corrosion po-tential experiences an increase in the corrosion rate, whereas the metal with the more positive corrosion potential experiences a decrease in the corrosion rate.[13] It should be emphatically stated that the $E_{couple}$ values only give an indication of the corrosivity of a solution toward the electrodes of interest.

From a Tafel plot analysis, it is possible to determine the $I_{couple}$ value, which is the corrosion cur-rent for the galvanic cell employed. As discussed, corrosion current values can be directly trans-lated into corrosion rates. This provides a direct relationship between the corrosion current measured and the influence of the corrosive environment on the metals of interest.

## 5    POTENTIODYNAMIC ANALYSIS USING INDIVIDUAL GALVANIC COUPLES

### 5.1    EXPERIMENTAL

Potentiodynamic determinations were made with solutions of varying corrosivity. Deionized (DI) water was the least corrosive of the solutions tested by virtue of its low conductivity. A single bulk quantity of tap water was sampled before testing began and was chosen based upon the increase in corrosivity associated with the greater number of ions in solution. Tap water samples were tested after the DI water was measured. An aqueous solution of 0.25% NaCl was chosen based upon the increased corrosivity resulting from the chloride ions. A solution of 0.25% NaCl to which 1.0% by weight of sodium nitrate ($NaNO_3$) was added to investigate the corrosion inhibiting properties of the nitrate containing species.[19] Finally, a solution of saturated potassium chloride (KCl) was chosen for its high degree of corrosivity. All solutions were made from analytical grade reagents purchased through the Sigma-Aldrich Company.

Each electrode was masked, with the exception of the galvanic couple under investigation, to avoid possible interferences from the other metals. Therefore, each galvanic couple consisted of a zinc counter electrode, a palladium/silver reference electrode, and one of the working elec-trodes. The working electrodes tested were made from metallic inks consisting of either tin, copper, iron, nickel, a gold/platinum alloy, or ruthenium oxide. Microstop® masking agent was applied to the surface of the ceramic substrate to the area to be masked, and was allowed to dry

for a minimum of 30 minutes before the next coat was applied. To ensure complete coverage, the area was coated a minimum of three times.

Electrochemical measurements were made with a Solartron 1286 potentiostat that was computer controlled with Corrware corrosion software. The instrumentation and software were chosen for the galvanic cell analysis since the equipment is standard for corrosion studies.

Two different sets of experimental parameters were chosen to investigate the metal couples. The first routine consisted of monitoring the OCP of the galvanic couple until a "steady state" was achieved. For the initial set of measurements, the potential was determined to be steady when the potential varied by no more than 5 mV for a period of at least 240 seconds. Potentiodynamic measurements were then initiated at a potential -100 mV of the OCP value and scanned at a rate of 0.167 mV/sec to a final potential 100 mV positive of the OCP. These parameters were chosen to avoid interferences to the solution at the more negative potential values and corrosion of the metal surfaces at the more positive voltages.

A second set of data was gathered by monitoring the OCP measurements until the OCP values varied by no more than 5 mV for a period of 600 seconds (10 min.). Once the system was considered stable by this set of criteria, the potentiodynamic measurements were initiated at 250 mV negative of the OCP value obtained, and scanned at a rate of 0.167 mV/s toward a value 100 mV positive of the OCP value monitored. Thus, the second condition set relied on a greater time for stabilization, as well as an increased range of potentials measured.

## 5.2    RESULTS

### 5.2.1   RESULTS UNDER EXPERIMENTAL CONDITION SET NUMBER ONE

A sample OCP data set for the copper-zinc couple is shown in Figure 9. As depicted in the figure, the OCP values stabilize at potentials that are more active (negative) as the corrosivity of the solution is increased. As expected, the OCP values for the DI water were the most noble (positive). A logical progression to more active potentials is observed for tap water and 0.25% NaCl. Interestingly, the open circuit values obtained for the 0.25% NaCl solution with 1.0 % $NaNO_3$ (corrosion inhibitor) were initially very similar to the 0.25% NaCl sample with no inhibitor present. After about 2 minutes, the OCPs stabilized to potentials values that were more positive (less corrosive) than the values for the sample without the inhibitor. This may be indicative of the formation of a passive layer on the metal surface that protects it from corrosion.[18] The OCP values obtained in the saturated potassium chloride solution were the most active (negative) and showed an increase in noise indicative of the high corrosivity of the solution.

Once OCP values were determined to be stable, the potentiodynamic measurements were initiated at potentials 100mV negative of the open-circuit values obtained, and scanned to potentials 100 mV positive of the OCP (see Figure 10). Theoretically, the $E_{couple}$ values obtained from the potentiodynamic measurements should be equivalent to the open-circuit potential. For this set of samples, the $E_{couple}$ values were more active than the open-circuit values obtained prior to the potentiodynamic runs. Deviations from theoretical predication may have resulted from two factors. The first and most likely is that the system might not have become stable before the potentiody-

namic plots were initiated. In this case, open-circuit measurements could be run for a longer period of time before the potentiodynamic scans were initiated, resulting in a longer time required to collect data. The second problem may include the use of prohibitively fast scan rates. While the potentiodynamic measurements were lengthy for most remote sensing purposes, it is feared that the scan rate might overrun the kinetics of the slowly corroding system. It should be noted that the corrosion potentials do not give quantitative information regarding the corrosion rate of the sample. In essence, it gives a simplistic snapshot of the corrosion status at any given point in time. To be useful, the kinetics of the corrosion process must be deciphered through the determination of the corrosion current.[18] Through a Tafel analysis of the potentiodynamic plot, the corrosion current for the system can be determined from the slope of the anodic branch.

Figure 11 shows the $E_{couple}$ and $I_{couple}$ values for the galvanic cell consisting of a copper working electrode and zinc counter electrode. Both standards of measurements show the same trend of increasing corrosivity from the DI water, through the tap water and 0.25% NaCl solutions. The corrosion current was suppressed by the addition of the 1% $NaNO_3$ and increased greatly in the saturated KCl solution. The $I_{couple}$ values give a more realistic indication of corrosion rates for the electrodes of interest, than the $E_{couple}$ values previously discussed. For example, the corrosion current for tap water was significantly increased in comparison to the DI water. Furthermore, the corrosion current for the solution of KCl was significantly larger than that for the other samples, as would be expected for high chloride containing solutions. The Ni, Sn, and Fe electrodes gave unexpected results.

## 5.2.2   RESULTS UNDER EXPERIMENTAL CONDITION SET NUMBER TWO

### 5.2.2.1 RESULTS FOR DIFFERENT GALVANIC CELLS MEASURED

An optimized set of parameters was required to collect measurements for all the electrodes. This necessitated running OCP measurements until the change in potential was no more than 5 mV for a period of at least 10 minutes. Once the OCP values were determined to be stable, the potentiodynamic plots were initiated at a potential 250 mV negative of the OCP and scanned at a rate of 0.167 mV/sec to a final measured potential 100 mV positive of the OCP.

Figure 12 shows a graphical representation of the $E_{couple}$ values for the different galvanic cell couples. From the data, the predictability of the measurements of corrosivity for the individual couples was poor for some of the galvanic cell couples. It is apparent that the copper-zinc cell was the only galvanic couple to give an appropriate response. This can be understood by considering the plethora of reactions contributing to the results as well as the properties of the surface of each metal. In this scenario, the two different metals have their own anodic and cathodic reactions. Thus, the anodic reactions of interest include the corrosion of each metal separately as well as the reduction reactions that occur in aqueous solutions. In the galvanic cell, the $E_{couple}$ values fall between the half-cell potential values of each metal, and it can be expected that each anodic and cathodic reaction will have an influence on the corrosive processes. It should be emphasized that the corrosion potential, while a mere indicator of corrosivity, does not correlate directly to the corrosivity of a solution, and therefore cannot be extrapolated into the corrosion rate. Other factors influencing the reproducibility of $E_{couple}$ and $I_{couple}$ measurements will be explained in the discussion section (paragraph 6).

Figure 13 shows a graphical representation of the $I_{couple}$ values for each galvanic cell measured under the second set of experimental conditions. The data was generated through a Tafel fit of the corresponding potentiodynamic scans. Once the data was obtained, two responses were of particular interest to the investigation. First, a proper relationship between the corrosivity of solution and corrosion current was particularly desirable, since a measure of corrosivity is what the investigation was based on. Second, a large magnitude of corrosion current is particularly appealing. In both cases, the only galvanic cell to routinely satisfy this set of conditions was the copper-zinc couple. It is important that the corrosion current follow the appropriate trend in corrosivity, especially for a set of solutions exhibiting such a wide range of corrosivities as those used in this study. From the calculated values of corrosion current, the only other electrode to come close to producing currents near the magnitude of the copper-zinc couple was the tin-zinc galvanic couple. This is most probably the result of the more noble half-cell potentials of copper and tin as opposed to the other metals used as working electrodes. Unfortunately, while the Sn electrode exhibited corrosion currents comparable in magnitude to those of the copper electrode, the trend in $I_{couple}$ did not follow the expected trend in corrosivity. It is reasonable to expect the trend in corrosivity to increase for the DI water, tap water, and 0.25% NaCl respectively. However, it is doubtful that the 1% addition of $NaNO_3$ would result in a decrease in corrosion current to the extent that the solution could be considered less corrosive than DI water. This argument also holds for the analysis of the KCl solution. The corrosion current measured was less than that for the DI water. From the data, it appears that when the 0.25% NaCl solution was run, corrosion products may have been left on the surface, reducing the corrosion current of the sodium nitrate inhibited sample, as well as the saturated potassium chloride containing solution. This observation illustrates the need to study how the copper-zinc couple responds when the surface of the electrode is allowed to pre-corrode, and remain in this state through the measurements, as opposed to being cleaned after each measurement.

## 5.2.2.2 COMPARISON OF CLEAN VS. NONCLEANED ELECTRODES

A comparison of a copper-zinc couple in which the electrode was cleaned between measurements and when it was not is shown in Figure 14. The data is instructive in that it is desirable that the electrodes give reproducible measurements for extended periods, without a need to recondition the electrode surface. Both sets of measurements were obtained using the same electrode. For the potentiodynamic response using cleaned electrodes, a silicon oxide and aluminum oxide abrasive was used to remove the corrosion products produced from the previous run. The OCP values were monitored until the potential of the system varied by no more than 5 mV for a period of at least 10 minutes. Once the OCPs were considered stable, the potentiodynamic measurements were initiated. The anodic potentiodynamic scan was initiated at 250 mV negative of the OCP and scanned at a rate of 0.167 mV/s to a potential 100 mV positive of the OCP.

A procedure was selected to make potentiodynamic measurements with the electrode that was not cleaned. Prior to the measurements (shown in Figure 14), the electrode was cleaned, and five potentiodynamic measurements were made with DI water as an electrolyte to precorrode the electrode. All successive measurements were made without cleaning the surface of the electrode and merely changing the electrolyte.

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The $I_{couple}$ values (Figure 14) obtained for the copper-zinc couple that was cleaned are similar to the prior measurements discussed. The 0.25% NaCl solution showed a marked increase in corrosion current (and corrosion rate) as compared to the DI water and tap water samples. When measurements were made with a 0.25% solution of NaCl with 1.0% $NaNO_3$, a decrease in corrosion current was observed as would be expected. Finally, the saturated KCl solution showed a marked increase in $I_{couple}$ values for the highly corrosive solution.

Measurements of DI and tap water were similar for both the cleaned and uncleaned electrodes. Unfortunately, as solutions of greater corrosivity were measured for the noncleaned electrode, a marked suppression in current was apparent. This can be explained by a buildup of corrosion products on the surface of the electrodes that inhibit the $I_{couple}$ values. Furthermore, it was not until measurements of saturated potassium chloride for the noncleaned galvanic cell were made that a marked increase in $I_{couple}$ values was seen. As indicated in Figure 14, deviations in the $I_{couple}$ values for the electrode that was not cleaned between runs would make the evaluation of corrosivity precarious at best. The analysis suggests that the electrodes be cleaned of corrosion products between measurements or that a disposable set of electrodes is engineered into the design of the sensing ceramic.

## 5.2.2.3 THE REPRODUCIBILITY OF GALVANIC MEASUREMENTS

The suppression of corrosion currents is an issue that must be addressed and is of concern with an actively corroding electrode. Specifically, it is desirable that measurements are reproducible. To investigate the reproducibility of the electrochemical measurements, potentiodynamic scans were run with DI water, tap water, 0.25% NaCl, 0.25% NaCl with 1.0% $NaNO_3$, and saturated KCl respectively. The experimental parameters used to investigate the reproducibility of measurements are the same as those used to compare the cleaned and noncleaned electrodes. All measurements monitored OCP values until the potential of the system varied by no more than 5 mV for a period of at least 10 minutes. Once the OCP's were considered stable, the potentiodynamic measurements were initiated. The anodic potentiodynamic scan was initiated at 250 mV negative of the OCP and scanned at a rate of 0.167 mV/s to a potential 100 mV positive of the OCP. These conditions were employed for a total of three measurements for each solution.

A summary of the experimental measurements for each electrode is depicted graphically in Figure 15. In essence, the trend in corrosivity as a function of solution tested is similar to that seen for the individual measurements previously discussed. As can be seen in Figure 15, there is a large deviation in corrosion current for saturated KCl. In general, the variation in measurements was large as indicated by the corrosion current values and their standard deviations in Table 1. The large deviations in $I_{couple}$ values may partly be the result of an inconsistent cleaning of the electrodes between measurements. Particularly problematic are the ridges and valleys present on the surface of the electrode that prevent the polishing agent from effectively cleaning the entire surface. Furthermore, the question remains as to whether the cleaning agent employed can effectively clean the surface of the electrode and bring it back to its original condition.

Figure 16 shows a graphical representation of the individual $I_{couple}$ values for the copper-zinc measurements and the variation in measurements between the representative samples. It is readily apparent from the data that the surface of the electrode is degrading with each measurement.

Except for the saturated KCl, the $I_{couple}$ values decrease successively for each measurement of the same solution. This indicates that the surface of the electrode was degrading and the polishing method employed was not suitable to bring the surface of the electrode back to a pristine (corrosion free) condition.

## 6    DISCUSSION

### 6.1    DISADVANTAGES IN THE ANALYSIS OF CORROSIVE ENVIRONMENTS WITH POTENIODYNAMIC MEASUREMENTS

The results indicated that a major disadvantage in the use of the potentiodynamic method for the analysis of corrosive analytes is the length of time needed to collect data. Each potentiodynamic scan requires that the system stabilize before the $I_{couple}$ and $E_{couple}$ values can be determined. The amount of time needed to collect data can vary by a wide margin. Unless this problem is addressed, a background corrosion potential that changes during the potentiodynamic measurements is present.[18] This is especially of concern with respect to the investigation of Martian soils. The rovers have a limited time of operation and simply cannot wait for numerous successive samples to stabilize. Doing so will interfere with the collection of data for other soil analyzing components. One can imagine the extent of the problem when it is realized that Bennett [14] used a 2-hour time lag before starting potentiodynamic measurements.

Another disadvantage is the length of time required to run the potentiodynamic scans. For the current study, a scan rate of 0.167 mV/sec was chosen. This equates to approximately 35 minutes to complete each scan. While this adds a great deal of time to each measurement, it is problematic with respect to the length of time that the working electrode remains in the corroding anodic region of the polarization scan. This makes potentiodynamic measurements deficient for kinetic-related corrosion studies.[18] Any time a potentiodynamic scan is run in the anodic region, the onset of corrosion is induced. This necessitates a rapid scan rate to limit corrosion on the electrode as well as limiting the anodic region of the potentiodynamic scan. In opposition to this requirement is the need for a fairly slow scan rate to limit charging on the surface of the electrode. Furthermore, the potentiodynamic technique necessitates sweep rates that are slow enough to attain steady-state results.

In general, it is desirable for the electrode to remain in its original preexposed state to make reproducible measurements. Limiting the anodic potential scan with reference to the open-circuit potential is also of concern. While it is best to limit corrosion on the surface of the electrode, potentiodynamic scans often necessitate the use of anodic scans which run 250 mV positive of the open-circuit values. This in effect can corrode the electrode to a degree that further hampers the reproducibility of measurements. In essence, the potentiodynamic methods employed are destructive to the surface of the electrode.

Of consequence to the galvanic technique under investigation and its use in an electrochemical multisensor is the formation of ionic products. For instance, potentiodynamic scans made with the copper electrode can convert the metallic copper to its ionic form. Complicating the issue for the galvanic cell analysis is plating that may occur on the surface of the electrodes as well. This is a serious problem for samples in the liquid state since ionic species easily travel from one elec-

trode to another. For example, when potentiodynamic scans are run, some of the copper is invariably converted from its metallic to ionic form as shown in Equation 15.

$$Cu^0 \rightarrow Cu^{+2} + 2e^-$$ (15)

The free ions are then available to plate out on the more reactive metallic zinc electrode through the reaction in Equation 16.

$$Zn(s) + Cu^{+2} \rightarrow Zn^{+2} + Cu(s)$$ (16)

This process can continue until the zinc electrode is completely fouled through copper plating or the copper ions in solution are completely converted from the ionic to metallic form.

Once produced, the ions can remain in solution to be detected by other components of the multisensor. This concept is more problematic when one considers the multiple metallic species used to form the galvanic cell array. When measurements are made in solution, ionic materials can easily move between the components of the multisensor, which may be detected by the CV electrodes or the ISEs. This necessitates the separation of individual galvanic cell components so other electrochemical components of the sensor are not influenced by the ionic species produced through the potentiodynamic scans. It is assumed that the problems of extraneous ions in solution would be less severe when investigating samples in the solid state, though experimentation has not been performed to support this hypothesis.

As outlined in the theoretical section of this paper, potentiodynamic scans are heavily dependent on the pH and oxygen content of the media. These two factors influence the potentiodynamic scans and unfortunately act as unknowns in the individual determination of species in solution. Consequently, potentiodynamic measurements to determine individual species are difficult without accounting for the pH and oxygen content in the media. In essence, both these factors influence the potentiodynamic scans because of the increased corrosivity of the solution or soils investigated, which causes corrosion of the metal electrodes.

The surface of the electrode is a topic that must be addressed in this discussion. Specifically, it is desirable for a metallic surface to have and retain as few imperfections as possible. It should be recognized that any material residing on the surface of the electrode can give extraneous electrochemical results. Though a number of different electrodes were tested, the copper working electrode was the only one to give reproducible results. This finding is probably not only the result of the metal studied but also has much to do with the physical characteristics of the electrode surface. As corrosion products are formed on the surface of the electrode, the current is influenced by the accumulated growth of corrosive contaminants. This results in the growth of an oxide layer with different electrochemical properties from that of the metal itself and results in an electrode surface that is constantly changing. This necessitates the use of an internal standard to act as a measure of the electrode degradation, pre-corroded electrodes which are run at very slow scan rates, or disposable electrodes. Figure 17 illustrates the surfaces for the Ni and Cu electrodes. As is apparent in the pictures, the nickel electrode has deeper and more numerous valleys, which trap corrosion products after each run. In general, Mears and Brown[20] have pointed out that the potential of a given electrolyte in solution may be affected by the composition, de-

formation, and treatment of the metal. Further problematic to potentiodynamic measurements are scratches and roughness of the surface of the metal, the shape of the specimen, and formation of films.[20]

Operationally, the determination of corrosion current from a Tafel analysis can be problematic. In order to successfully employ this technique, a sufficiently linear region of the potentiodynamic scan must be present. Unfortunately, it is not always possible to determine corrosion currents through a Tafel plot analysis. This most often results from the absence of linear regions, which are not always present, to allow Tafel plots to be extrapolated from potentiodynamic scans.[13] Further problematic is the limited diffusion of ionic products to and from the surface of the electrodes, as well as IR drop.[14] This helps to explain why an acceptable ranking of corrosive solutions was obtained only with solutions of widely varying corrosivity. When solutions of similar corrosivities were investigated, appropriate rankings of corrosivity were not always possible.

## 6.2 PROPOSED USES FOR THE POTENTIODYNAMIC METHOD TO ANALYZE CORROSIVE ENVIRONMENTS

The concept of the galvanic analysis of corrosive environments has been studied by Agarwala[21-24]. Though similar to this effort, the work was based upon the measurement of galvanic current. In essence, the galvanic current was correlated with the corrosive nature of the environment. The investigations concluded that the metal combinations that proved most sensitive for the analysis of slightly corrosive environments was the Au-Cd couple. In contrast, environments that were more corrosive were best studied with a Au-Ni galvanic couple. This technique utilizes the current produced between the galvanic couple without artificially inducing corrosion through an applied potential.

It should be understood that electrochemical measurements often do not give a reasonable measure of service performance.[18] It can be hypothesized that the analysis of corrosive environments can be better understood not only through the measurement of galvanic current but through the implementation of other electrochemical techniques as well. Linear polarization is a particularly appealing electrochemical technique since the potentials are applied near the OCP values. This significantly limits the corrosion to the surface of the electrodes. Once the data reasonably suggests that corrosivity is an issue, the potentiodynamic methods in this report can be employed as an additional method of analysis.

## 7 CONCLUSIONS

This investigation centered upon the development of a galvanic sensor array as an addition to an electrochemical multisensor developed for the analysis of Martian soil. A Tafel plot fit was used to determine $I_{couple}$ values, which are proportional to the corrosion rate for the metals studied in solutions of different corrosivities. It was determined that the Cu-Zn galvanic couple gave the best results among the metals investigated. This finding is probably not only the result of the metals studied but also has much to do with the physical characteristics of the electrode surface.

Results obtained for the galvanic cell array through the potentiodynamic analysis of corrosive solutions indicated that a major disadvantage in their use is the length of time needed to collect data.

A comparison of results for the copper-zinc couple in which the electrode was cleaned between measurements and when it was not suggested that the electrodes be cleaned of corrosion products between measurements or that a disposable set of electrodes is engineered into the design of the sensing ceramic. However, the question remains as to whether the cleaning process can be performed in a reproducible manner.

Visual observations revealed fouling of electrodes that was caused by the plating of ions generated on neighboring galvanic electrodes. This will require the separation of individual galvanic cell components so that other electrochemical components of the sensor are not influenced by other ionic species produced through the potentiodynamic scans.

The irregular surface of the electrode, combined with the corrosion products produced through the potentiodynamic method, had a significant influence on the electrochemical results. The experimental evidence suggests that the use of a smooth electrode surface, combined with other electrochemical techniques (measurement of galvanic current and linear polarization), might prove useful to improve the characterization of corrosive environments.

## 8      REFERENCES

(1)     Koch, V. H., Brongers, M.P.H., Thompson, N.G., Virmani, P.H., Payer, J.H. *Supplement to Materials Performance* 2002, 1-12.
(2)     Baker, V. R. *Nature* 2001, *412*, 228-36.
(3)     Jakoskey, B. M.; Jones, J. H. *Nature* 1994, *370*, 328-329.
(4)     Ward, A. W.; et al. *Journal of Geophysical Research* 1999, *104*, 8555-8571.
(5)     Golombek, M. P. *Science* 1999, *283*, 1470-1.
(6)     West, S. J.; Frant, M. S.; Wen, X.; Geis, R.; Herdan, J.; Gillette, T.; Hecht, M. H.; Schubert, W.; Grannan, S.; Kounaves, S. P. *Am Lab* 1999, *31*, 48-54.
(7)     Bell, J. F. *Journal of Geophysical Research* 2000, *105*, 1721-1755.
(8)     Kieffer, H. H. *Mars*; University of Arizona Press: Tucson, AZ 1992.
(9)     Buehler, M. G.; Kuhlman, G. M.; Keymeulen, D.; Kounaves, S. P. 2002 IEEE Aerospace Conference, Big Sky, MT, 2002; p 407-416.
(10)    Skoog, D. A.; Leary, J. J. *Principles of Instrumental Analysis*; 4th ed.; Saunders College Pub.: Fort Worth, TX 1992.
(11)    Buehler, M. G.; Kounaves, S. P.; Martin, D. P.; West, S. J.; Kuhlman, G. M. 2001 IEEE Aerospace Conference, Mar 10-17 2001, Big Sky, MT 2001; p 1331-1337.
(12)    Kounaves, S. P.; Buehler, M. G.; Hecht, M. H.; West, S. J. In *ACS Symposium Series*; Taillefert, M., Rozen, T. F., Eds.; American Chemical Society: Washington, D.C., 2002; Vol. 11.
(13)    Stansbury, E. E.; Buchanan, R. A. *Fundamentals of Electrochemical Corrosion*; ASM International: Materials Park, OH, 2000.
(14)    Bennett, D. C., University of Connecticut, 1973.

(15) Hannemann, R. J. *Semiconductor Packaging: A Multidisciplinary Approach*; J. Wiley: New York, 1994.

(16) Stern, M. *J. Electrochem. Soc.* 1958, *105*, 638-647.

(17) Stern, M.; Geary, A. L. *J. Electrochem. Soc.* 1957, *104*, 56-63.

(18) Jones, D. A. *Principles and Prevention of Corrosion*; 2nd ed.; Prentice Hall: Englewood Cliffs, NJ, 1996.

(19) Yang, L.; Sridhar, N.; Dunn, D. S. *Corrosion* 2002, *58*, 1004-1014.

(20) Mears, R. B.; Brown, R. H. *Industrial Engineering Chemistry* 1941, *33*, 1001.

(21) Agarwala, V. S. 1992 Tri-Service Conference, Watertown, MA 1992.

(22) Agarwala, V. S. *Sensors for Corrosion Detection and Monitoring of Hidden Areas*; The Electrochemical Society: Pennington, NJ 1993.

(23) Agarwala, V. S.; Ahmad, S. CORROSION/2000, Houston, TX, 2000; Paper No. 271.

(24) Agarwala, V. S.; Fabiszewiski, A. CORROSION/94, Houston, TX, 1994; Paper No. 342.

## 9    TABLES

Table 1 – Mean and standard deviations for the $I_{couple}$ values for the copper-zinc galvanic couple

| | Mean (X $10^{-8}$ Amps) | Standard Deviation (X $10^{-8}$ Amps) |
|---|---|---|
| DI Water | 1.804 | 0.850 |
| Tap Water | 2.021 | 0.509 |
| 0.25% NaCl | 5.861 | 0.408 |
| 0.25% NaCl + 1.0% NaNO$_3$ | 2.868 | 1.109 |
| Saturated KCl | 10.720 | 5.436 |

(OCP $\Delta E < 5$mv for 10 minutes, PDS from –250 mV vs. OCP to 100 mV of OCP)

10    FIGURES



Figure 1 – Gullies in crater at $42.4^0$S, $158.2^0$W - NASA/JPL release no. MOC2-320, 7 October 2002
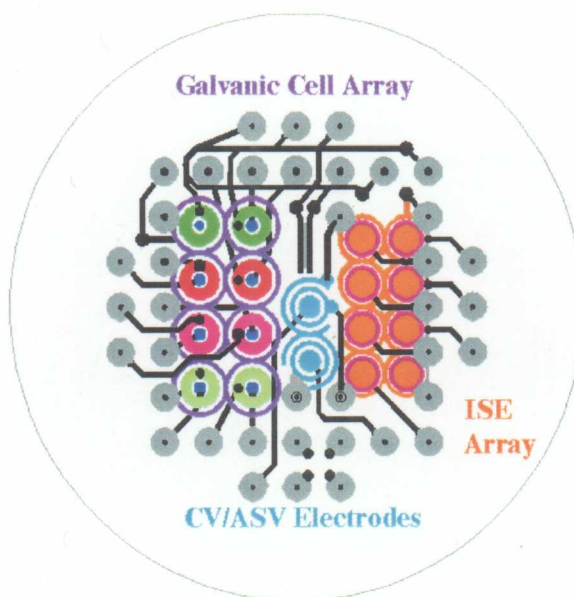


Figure 2 – Schematic of individual sensing components (galvanic cell array on the left, CV/ASV electrodes in the center [light blue], and ISE electrodes on the right [orange])
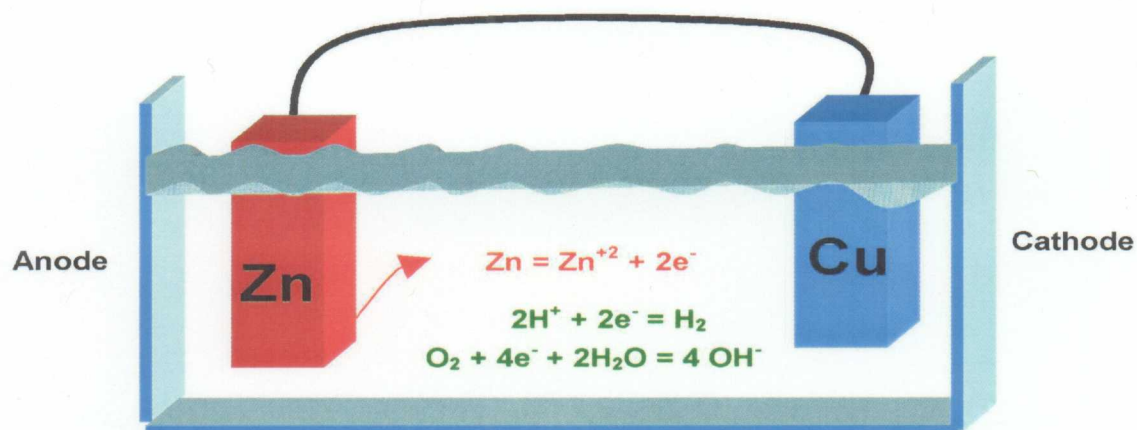
Figure 3 – Galvanic corrosion
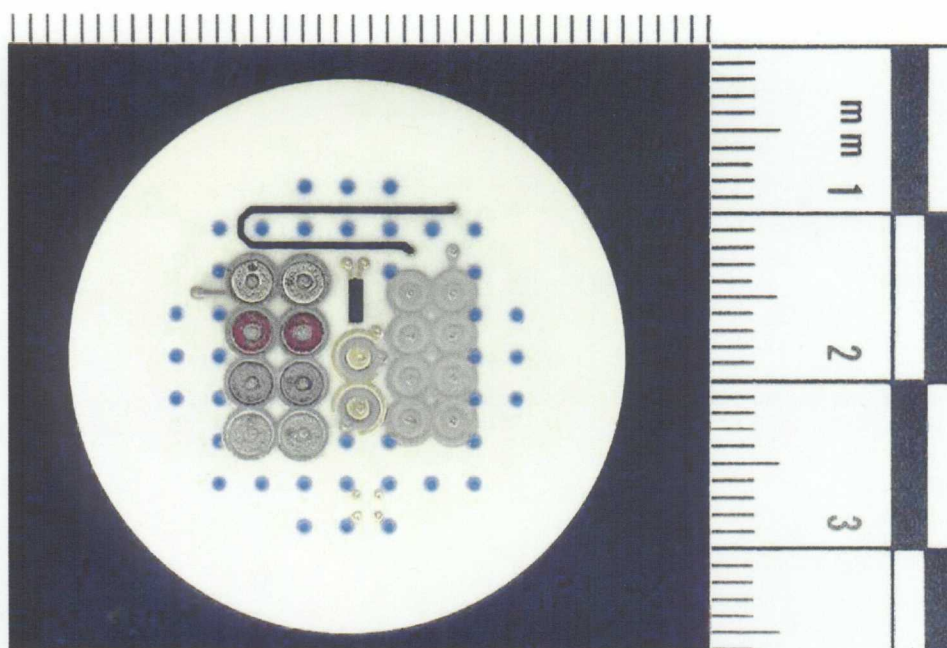


Figure 4 – Top side of 3.3-cm-diameter ceramic substrate showing individual sensor components
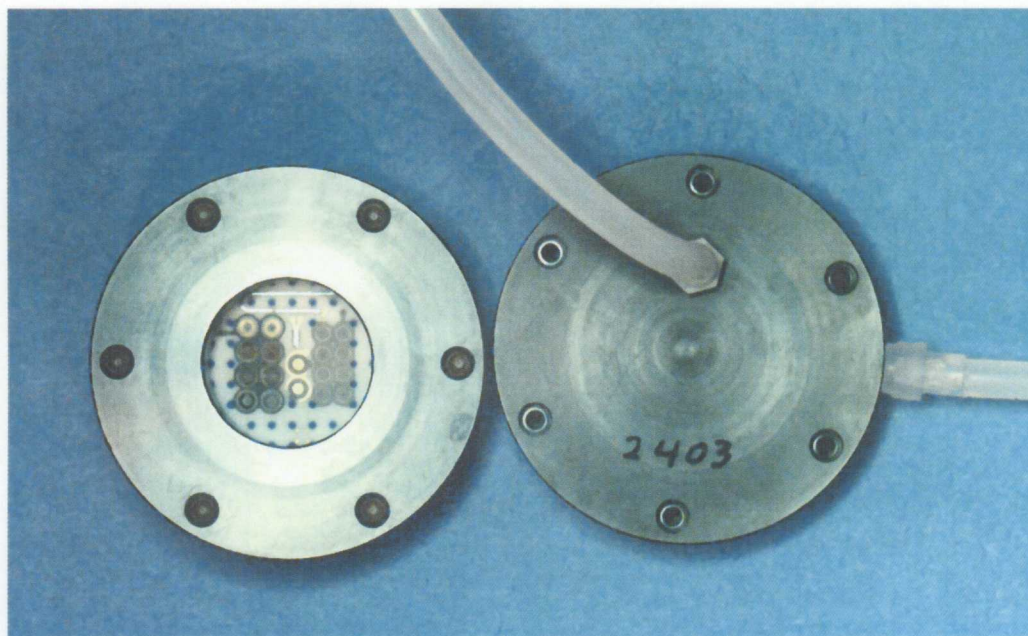
Figure 5 – Soil chamber (left) and fluidics chamber (right)
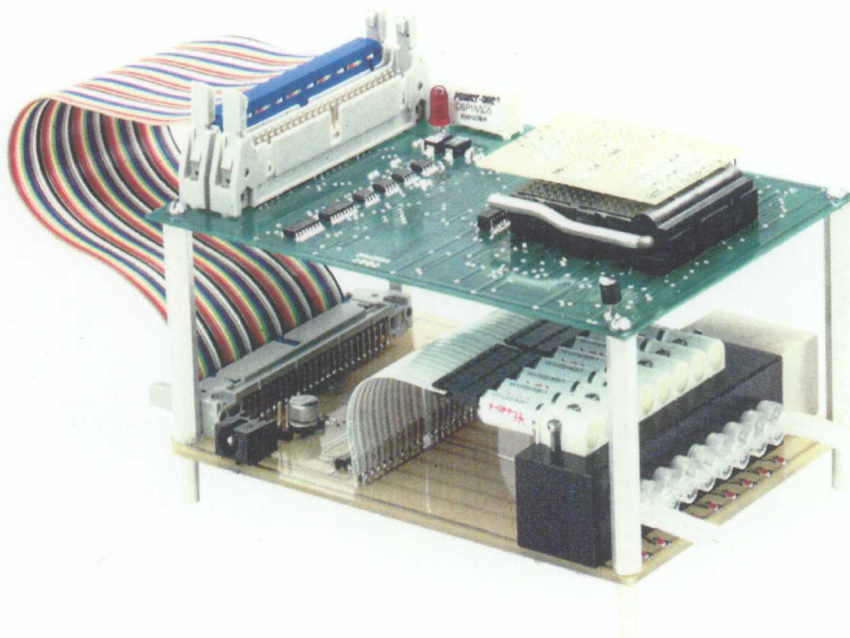


Figure 6 – Electronics board (top) and fluidics board (bottom)
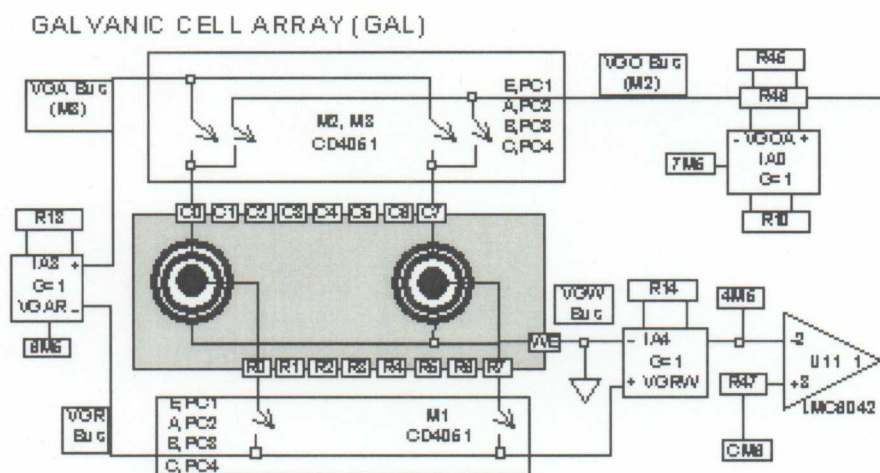
Figure 7 – Galvanic cell electronics
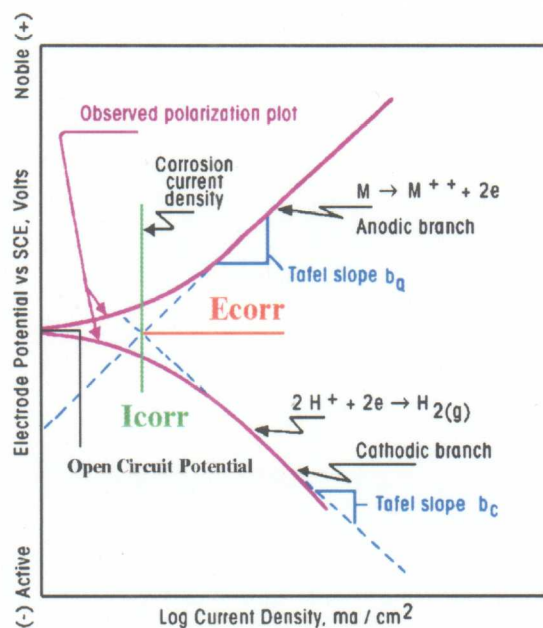


Figure 8 – Hypothetical potentiodynamic polarization plot of a metal in an acidic solution
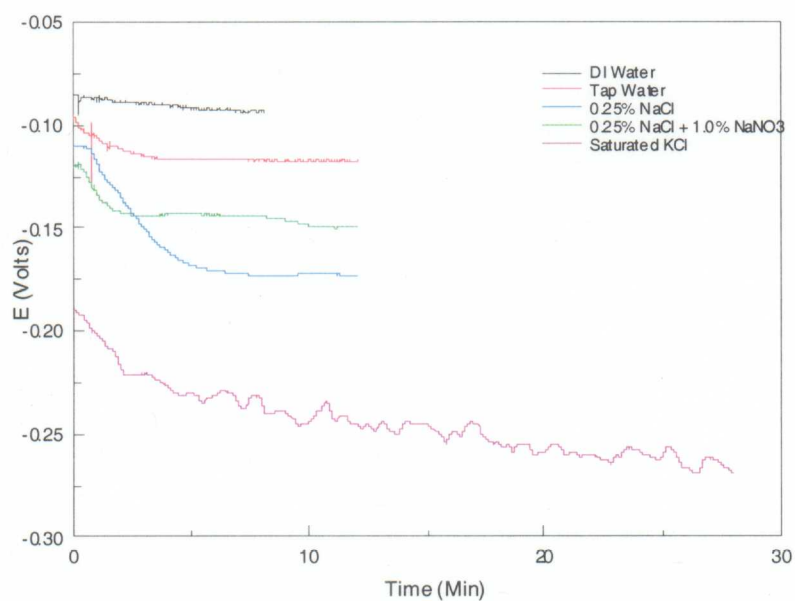
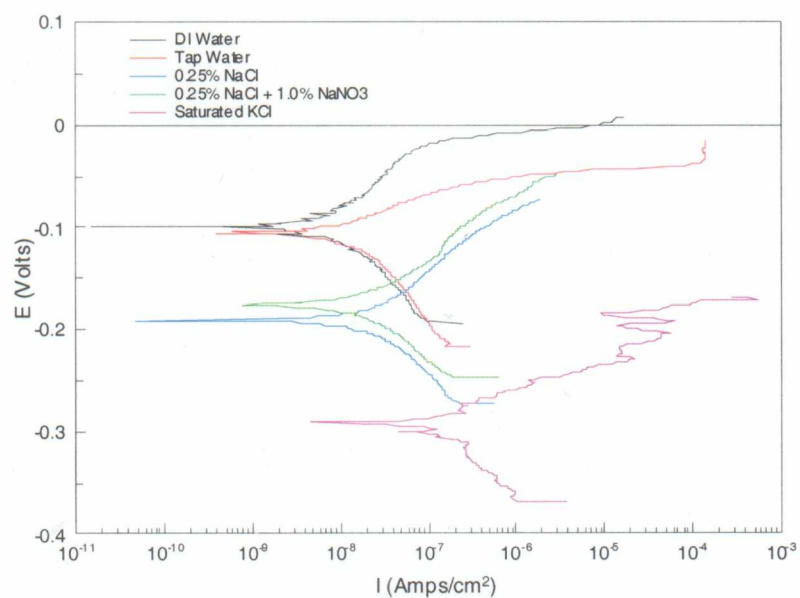Figure 9 – Open-circuit potential measurements for galvanic couple with
Cu working electrode and Zn counter electrode



Figure 10 – Potentiodynamic measurements for galvanic couple with
Cu working electrode and Zn counter electrode
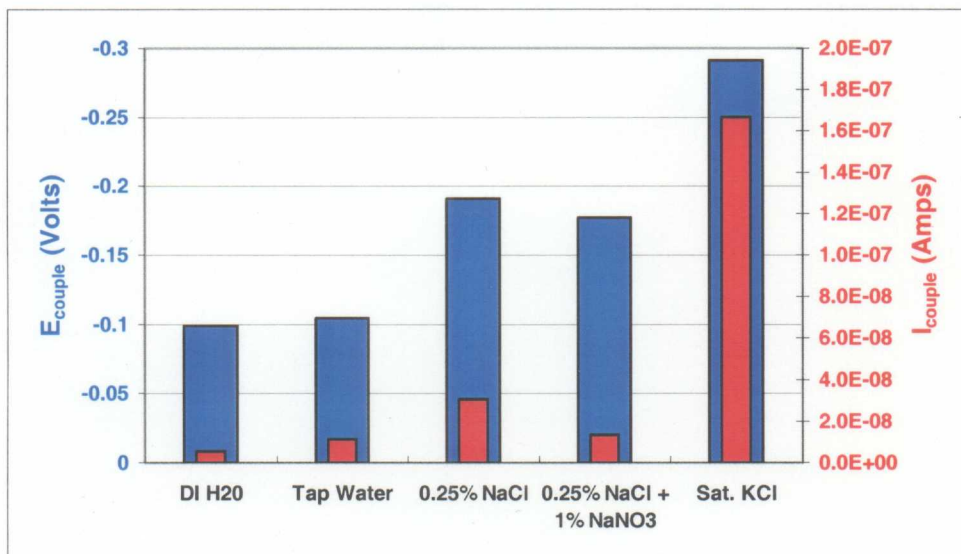
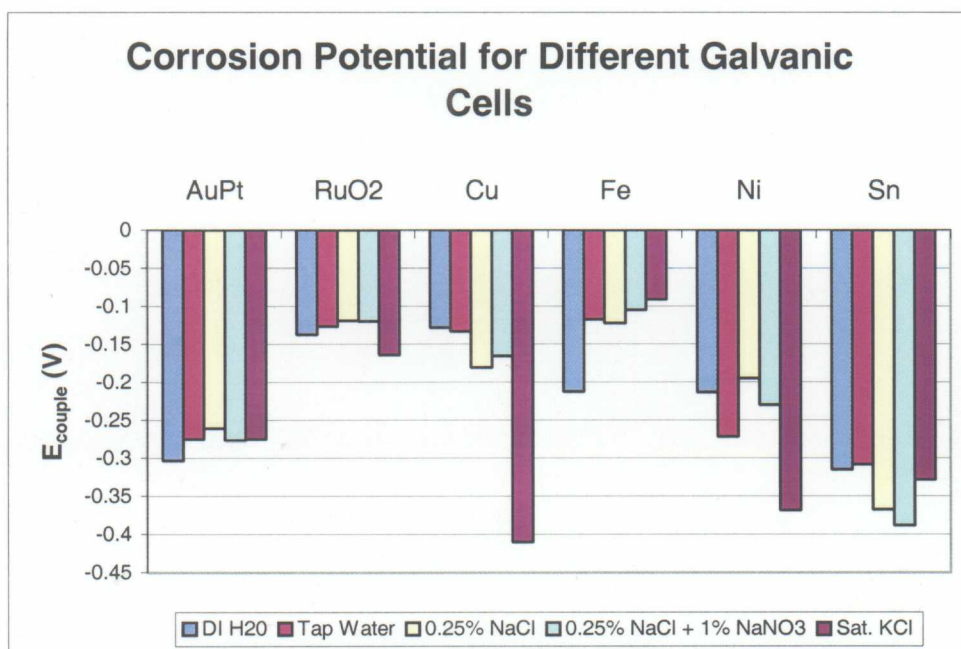Figure 11 – $E_{couple}$ and $I_{couple}$ values for Cu working electrode and Zn counter electrode



Figure 12 – $E_{couple}$ values for galvanic cell arrays
(OCP $\Delta E < 5$ mv for 10 minutes, PDS from –250 mV vs. OCP to 100 mV of OCP)
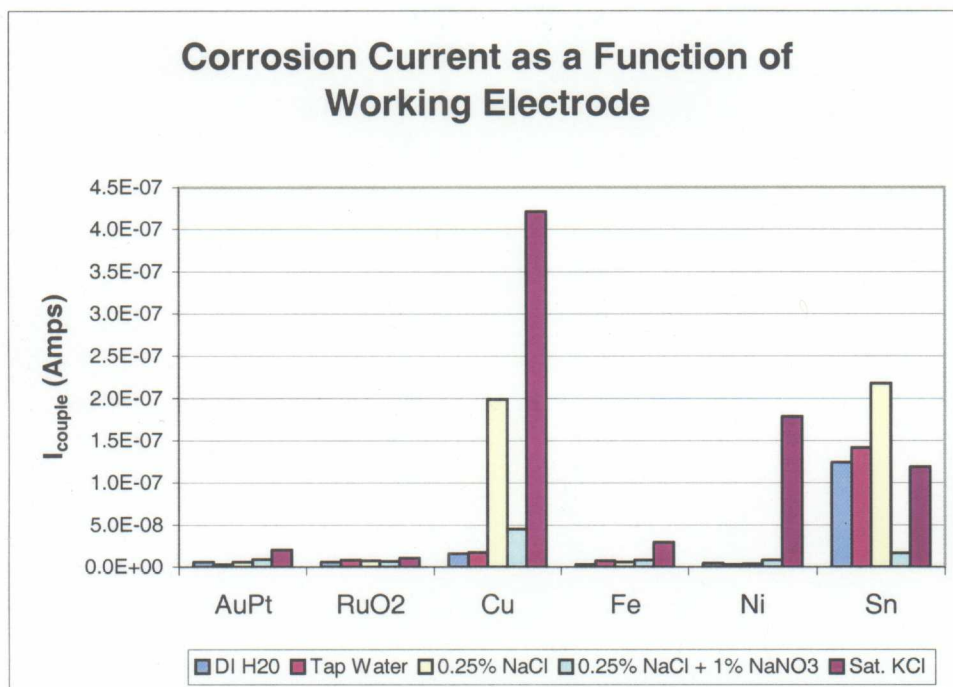
Figure 13 – $I_{couple}$ values for galvanic cell arrays
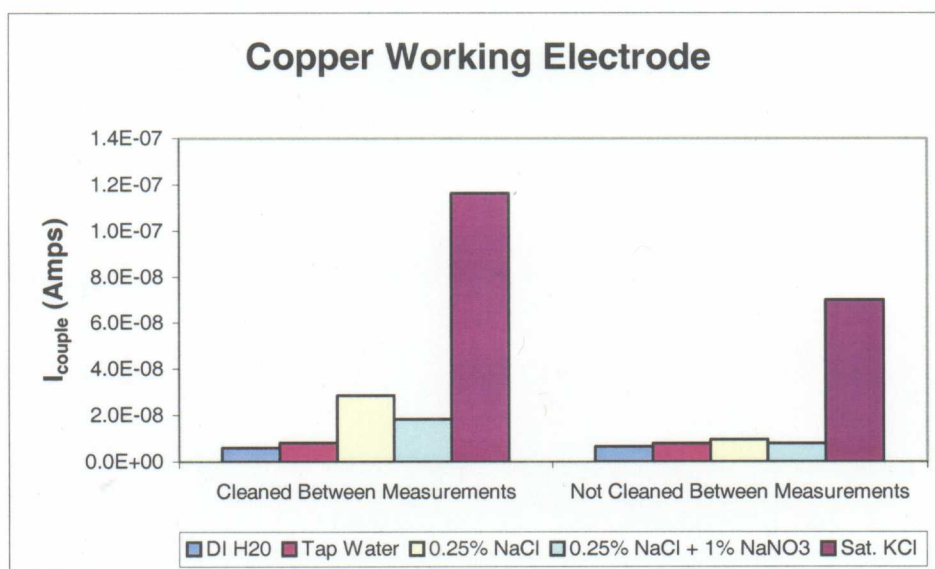(OCP $\Delta E$ < 5 mv for 10 minutes, PDS from –250 mV vs. OCP to 100 mV of OCP)



Figure 14 – $I_{couple}$ values for Cu-Zn galvanic electrodes
(OCP $\Delta E$ < 5 mv for 10 minutes, PDS from –250 mV vs. OCP to 100 mV of OCP)

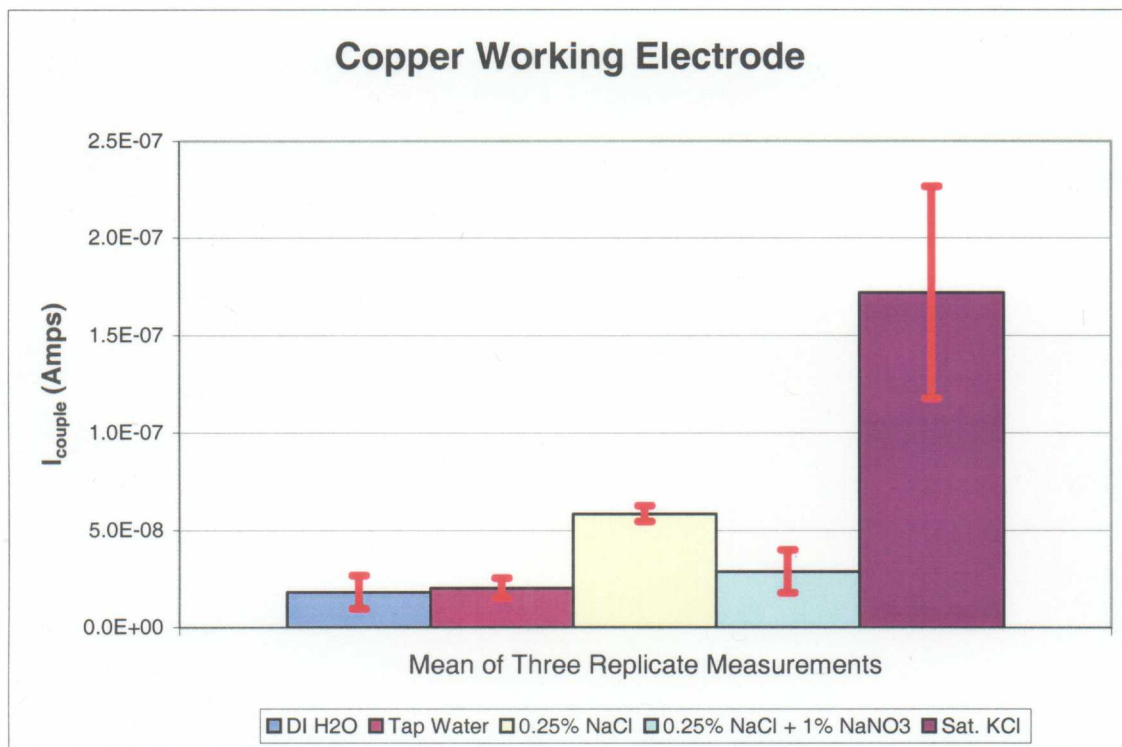Figure 15 – $I_{couple}$ values for Cu-Zn galvanic electrodes
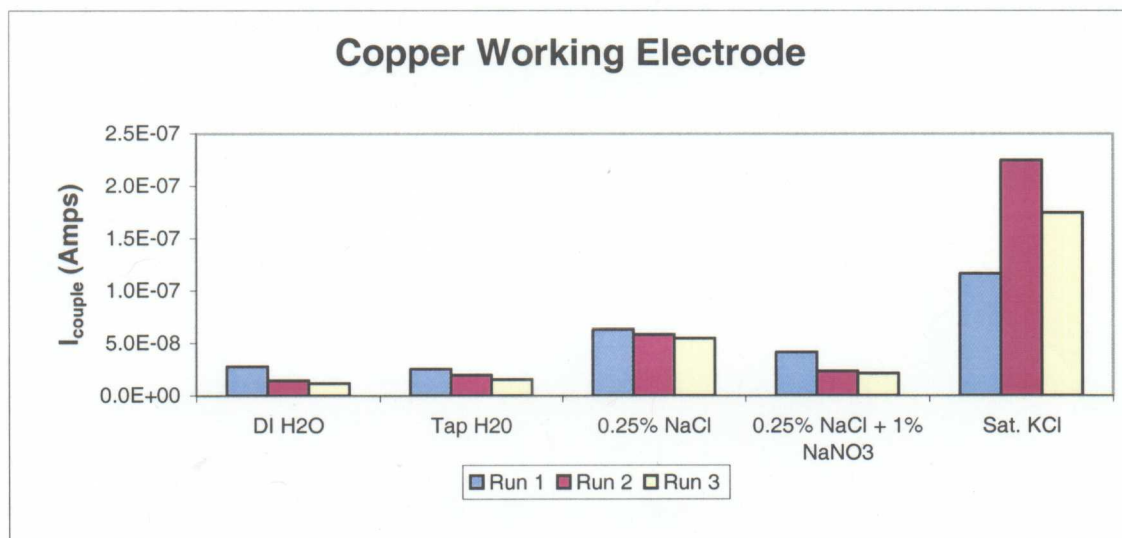(OCP $\Delta E < 5$ mv for 10 minutes, PDS from $-250$ mV vs. OCP to 100 mV of OCP)



Figure 16 – Three replicate $I_{couple}$ measurements for the Cu-Zn galvanic couple
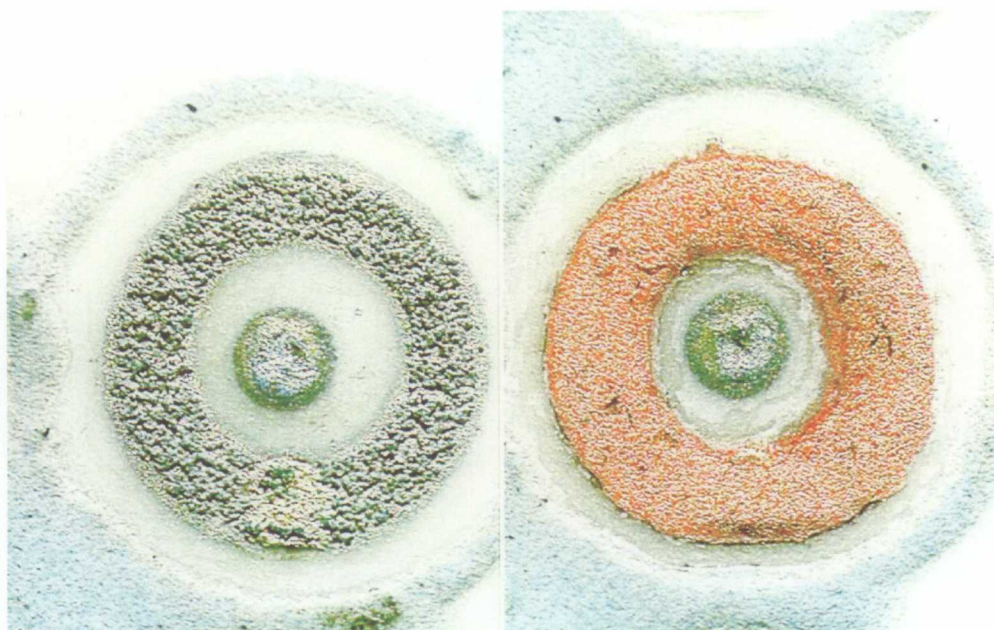(OCP $\Delta E < 5$mv for 10 minutes, PDS from $-250$ mV vs. OCP to 100 mV of OCP)

Figure 17 – Ni working electrode (silver ring on left) and Cu working electrode (orange ring on right)

# REPORT DOCUMENTATION PAGE

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13. ABSTRACT (Maximum 200 words)

An initial investigation into the response of the individual galvanic couples was conducted using potentiodynamic polarization measurements of solutions under conditions of varying corrosivity. It is hypothesized that the differing electrodes may provide a means to further investigate the corrosive nature of the analyte through genetic algorithms and pattern recognition techniques. The robust design of the electrochemical sensor makes its utilization in space exploration particularly attractive. Since the electrodes are fired on a ceramic substrate at 900 °C, they may be one of the most rugged sensors available for the anticipated usage.

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